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BIODEGRADABILITY OF JP-8 FUEL IN THE AQUATIC ENVIRONMENT

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INTRODUCTION

JP-8 is a versatile kerosene–based aviation turbine fuel and is interchanged under NATO Code Number F-34. The U.S. military and NATO Nations have used JP-8 fuel for several decades as the single fuel on the battlefield. Its composition is essentially identical to JET A-1, used by commercial airlines for worldwide operations, except for the presence of an additive package consisting of a very small amount of a fuel system icing inhibitor, corrosion inhibitor/lubricity improver, and static dissipator additive (SDA). Under the single fuel concept for the military air and land battlefield operations, the U.S. Army also uses JP-8 for all diesel and gas turbine powered ground vehicles and equipment. JP-8 is currently procured under MIL-DTL-83133[1] in U.S.A and the other nations procure it under NATO STANAG 3747 Guide Specifications[2].

As with the other aviation kerosene based turbine fuels, JP-8 fuel is a mixture of aliphatic, aromatic and substituted naphthalene hydrocarbon compounds. It is a very clean fuel and does not react or emulsify with water. These typical physical properties prevent the occurrence of any fuel system corrosion and reduce potential for microbiological growth when compared to diesel fuel. Its fuel system icing inhibitor (FSII) also affords increased protection against microbiological growth since FSII in addition to being an icing inhibitor also acts as a bio-stat. This is important for equipment like the ABRAMS tank, where fuel deterioration and microbiological contamination in the front fuel cell have been and are continuing problems[3].

Recently, there has been and continues to be a concern with the microbiological contamination in JP-8 fuel. Many military installations often observe microorganism growth in JP-8 fuel storage tanks due to the presence of water contamination. This microorganism growth can sometimes lead to operational problems such as cloudy fuel, filter blocking, and corrosion-related problem as well as the generation of unpleasant odors. On the other hand, JP-8 fuel is currently defined as hazardous material and if spilled, it must be cleaned up to avoid contamination of the soil and ground water. This problem can create a high clean up cost and requires a long period for removing fuel contamination from spilled sites. In this case, biodegradable fuels are desired for the future to resolve this environmental problem.

To address those concerns, a study for determining the environmental fate and biodegradation of JP-8 fuel under the aquatic environments was undertaken. This paper

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reviews the microbiology on hydrocarbon fuels, and discusses the results of biodegradation tests and the efficacy of biocide on JP-8 fuel, and their resultant findings.

OVERVIEW OF MICROBIOLOGY ON HYDROCARBON FUELS

Microbiology generally deals with unicellular microscopic organisms. All their life processes are performed within a single cell. Like other larger organisms, they need the elements carbon, nitrogen, and phosphorus in order to build cell structure. Water is required for the passage of nutrients and waste materials across the cell wall of the microorganism. In addition, certain elements such as sulfur, iron and manganese, are required in trace quantities for the production and functioning of enzymes needed for uptake and breakdown of nutrients. The microorganisms causing problems in the hydrocarbon based fuels can be classified into three main groups as follow[4]:

- Bacteria are unicellular organisms which are capable of living on wide variety of organic materials. They range in metabolism from heterotrophic (living on organic carbon compounds) to lithographic (using inorganic compounds as sources of energy) and phototropic (using sunlight as a source of energy). They generally reproduce by dividing into two equal daughter cells.

- Fungi are more complex organisms and can exist as either filamentous forms or as unicellular organisms. They are all dependent on organic carbon as a source of energy.

- Algae are all photosynthesis organisms, which use sunlight as a source of energy and carbon dioxide from atmosphere as a source of carbon for cell growth. Generally, these microorganisms do not create any major problem in closed fuel tanks.

The life and growth of these microorganisms often depends on the source of food chain, toxicity, and the surrounding environment. Most microorganisms found in fuel are bacteria and fungi. These microorganism growths are usually concentrated at the fuel-water interface. The presence of a free water layer in contact with the hydrocarbon layer results in greater growth, compared to a system where the water is emulsified within the hydrocarbon fuels. In many cases, the hydrocarbon based fuel provides a source of carbon for the growth and reproduction of organisms. Some organisms need air to grow (i.e., aerobic organisms), while others grow only in absence of air (i.e., anaerobic organisms). In addition to food and water, microorganisms also need certain elemental nutrients. Most fuels provide these elemental nutrients. Microbial contamination occurring in the fuel storage and dispensing systems can, as mentioned previously, create many problems. The solids formed by biomass are very effective in plugging fuel filters. Some microorganisms also generate acidic by-products that can accelerate metal corrosion[5]. To control the growth of microorganism, some toxic chemicals such as biocides are currently used to sterilize/kill organisms. Even if the biocide effectively

stops this microbiological growth, it still may be necessary to remove the accumulated biomass residue/debris to avoid filter plugging. The most practical way to avoid microbiological growth is keeping the amount of free water in a fuel storage tank as low as possible.

BIODEGRADATION TEST

Biodegradation is a naturally occurring process by the action of microorganisms. In the presence of oxygen, nitrogen, phosphorous, and trace minerals, organic pollutants can support microbial growth and are converted into a series of oxidation products that generally conclude with carbon dioxide and water. The biodegradation test method adopted in this study follows the ASTM D5864, "Standard Test Method for Determining Aerobic Biodegradation of Lubricants and Their components". Recently, ASTM D-12 Subcommittee on Environmental Standard of Lubricants has developed this biodegradation test method based on the Organization for Economic Co-Operation and Development (OECD) 301B, Modified Sturn Test which closely simulates the wastewater biotreatment conditions. The test method was originally designed to determine the degree of aerobic aquatic biodegradation of hydrocarbon materials on exposure to inoculums under laboratory conditions. In this test, the biodegradability of hydrocarbon based fuel is expressed as the percentage of maximum (theoretical) carbon conversion (or carbon dioxide generation) under well–controlled conditions for a period of 28 days.

Test Sample: A total of five samples were selected for the biodegradation test. To draw a baseline of this study, JET A and JET A-1 fuels were selected along with JP-8. As mentioned before, JET A-1 is essentially identical to JP-8 except for three additives required in JP-8. This aviation fuel (i.e., JET A-1) is the standard fuel used by all commercial airline companies worldwide, except within U.S.A. where JET A is principally used, the difference being only in freezing point requirements. JET A allows down to as low as -40 °C, while JET A-1 allows down to as low as-47 °C. Both fuels are kerosene based with their compositions being very similar to JP-8. In addition, diesel fuel was also selected for comparison with JP-8 because it (i.e., diesel fuel) has a history of microbiological growth and related problems in storage tanks. A reference bio-based product (i.e., canola oil) was also selected to control the microbiological growth in the biodegradation test. The typical properties of these selected fuels are summarized in Table 1.

Test Apparatus: A schematic diagram of the biodegradation test apparatus for ASTM D5864 is shown in Figure 1. This test apparatus was a slightly modified for the study. It consists of four separate units: the air supply/carbon-dioxide scrubbing system, the incubation/biodegradation batch reactor, a carbon-dioxide collector, and a titrator. Both the carbon-dioxide scrubbing and the biodegradation units utilize Erlenmeyer flasks. To eliminate other carbon sources except the test lubricant, CO_2-free air is needed for the biodegradation test. A laboratory compressed air supply was attached directly to the

carbon dioxide scrubbing system to produce CO_2-free air. The scrubbing system uses cascade flasks: two flasks containing 10 M potassium hydroxide (KOH) solution and two flasks containing 0.025 M barium hydroxide $Ba(OH)_2$ solution. To ensure the desired aerobic environment, the test solution containing the test fuel was fully agitated using a variable speed magnetic stirrer. In order to conduct multiple tests for performance comparison, ten separated identical biodegradation batch reactors were connected as seen in Figure 1. Each reactor can be independently and flexibly operated for aquatic biodegradation tests.

Table 1. Physical Properties and Chemical Compositions for Tested Fuels

Property	JET A	JET A-1	JP-8	Diesel Fuel (DL-2)
Density, lb/gal	6.482	6.377	6.652	7.111
Viscosity @40 °C, cSt	1.4	1.4	1.3	2.8
Sulfur, % mass	0.04	0.09	0.049	0.02
Freezing point , °C	-45.9	-49.5	-57	-13.9
Water content	nil	nil	nil	nil
Fuel Type	Kerosene	Kerosene	Kerosene	Distillate
Aromatic, % vol.	20.2	19.9	16.6	9.6
Olefin, % vol.	3.3	3.2	1.8	3.7
Saturates, %	76.5	76.9	81.6	86.7
Total Carbon content ,%	87.03	86.67	86.13	87.19
Additives Added	None	None	Corrosion inhibitor, FSII, SDA,	Various additives such as cetane improver, etc.
Sample Code Number	PQ-0056-03	FL-11824-03	PQ-0005-02	FL-11828-03

Test Procedure: Prior to the test, the test solutions were prepared according to the ASTM D5864 test procedure. Initially, five stock solutions for the test medium were prepared: ammonium sulfate solution (40 g/L), calcium chloride solution (27.5 g/L), ferric chloride solution (0.25 g/L), magnesium sulfate solution (22.5 g/L), and phosphate buffer (made of 8.5 g potassium dihydrogen, 21.7 g potassium monohydrogen phosphate, 33.4 g sodium monohydrogen phosphate, and 1.7 g ammonium chloride) It should be noted that these solutions do not contain any carbon material in order to avoid an extra source of carbon dioxide production. To permit a positive control as well as a fair comparison, canola oil was used as the reference sample. This oil has been identified to be a high biodegradable material. To determine the theoretical CO_2 evolution, the initial carbon content of the tested fuels was measured using a carbon analyzer.

The sewage inoculums (i.e., bacteria, yeast, fungi) were carefully prepared from the mixed liquor (approximately 1 liter) of activated sludge provided by a local wastewater treatment plant. These sewage inoculums were freshly collected from the biotreatment processing pool of the plant. It was fresh and contained the proper microorganisms for treating regular wastewater. In our laboratory, the total number of bacteria and fungi were observed and counted using the Easicult Bacteria Counting Kit[6]. This test kit is commonly used for measuring the growth of bacteria in an industrial process, such as cutting fluids, etc. To avoid carry-over of sludge solids which might interfere with the measurement of CO_2 production, the sewage inoculums was homogenized by a blender and aerated until ready for use.

A total of ten test flasks were used for the biodegradation tests. Six flasks were designed for the test samples, two flasks as positive controls (baseline reference sample: canola oil), and the remaining two flasks as blank controls. To prepare a one-percent inoculums solution, 2,470 mL of distilled water was added to each 4 L Erlenmeyer flask. The following stock solutions (i.e., concentration was explained earlier) were added to the test flasks: 3 mL each of ammonium sulfate, magnesium sulfate, and calcium chloride; 30 mL of phosphate buffer; and 12 mL of ferric chloride stock solution. After all stock solutions were mixed and diluted in the 4 L Erlenmeyer flasks, 30 mL of the activated sludge inoculums mentioned earlier was added to the test solution.

To purge the CO_2 gas that might have migrated from the room air of the laboratory during the inoculums solution preparation period, the test flasks were aerated with CO_2-free air for 24 hours. Then, three CO_2 collectors filled with 100 mL of 0.0125 M Ba $(OH)_2$ solution were connected in series to the downstream of each 4 L Erlenmeyer flask. Before adding the test (or reference) fluid samples, the pH values of the test solutions were all adjusted to 6.5 - 7.5 using HCl or NaOH solutions. About 80 mg of the test fluid sample was added into each of the six test flasks. Canola oil was also added into the duplicate positive control flasks. It is noted that the duplicate blank control flasks were free of test fluids. Then, the distilled water was added to maintain a final volume of 3 liters in each 4 L flask. All test flasks were tightly stoppered and maintained at 20 - 25 °C. The magnetic stirrer was kept at approximately 200 rpm. The volumetric flow rate of CO_2-free air to each test flask was maintained at 50 to 100 mL/min. It should be noted that each experiment included duplicate control flasks and duplicates of each test fluid sample. During the test, the test room was kept in complete darkness. This measure was necessary to prevent photo degradation of the test substance and the growth of photosynthesis bacteria and algae.

To measure carbon dioxide production during a predetermined test period, the CO_2 collector nearest the 4 L Erlenmeyer flask was removed for titration and calculations. The remaining two collectors were moved up one place closer to the 4 L Erlenmeyer flask and a new collector filled with 100 mL of fresh 0.0125 M Ba $(OH)_2$ was placed at the far end of the series. Titration was performed every day for the first 10 days and then every other day for the remaining 18 days or until a plateau of CO_2 evolution was reached. The end point used for automatic titration was set at pH 7. Once the CO_2 evolution has reached a plateau, the pH of the test solutions were measured and added 1 mL of HCl into the test

solutions to decompose the inorganic carbonate and to release trapped CO_2 for a final titration. Data obtained from the titration were converted to the amount of CO_2 production using an equation specified by the method.

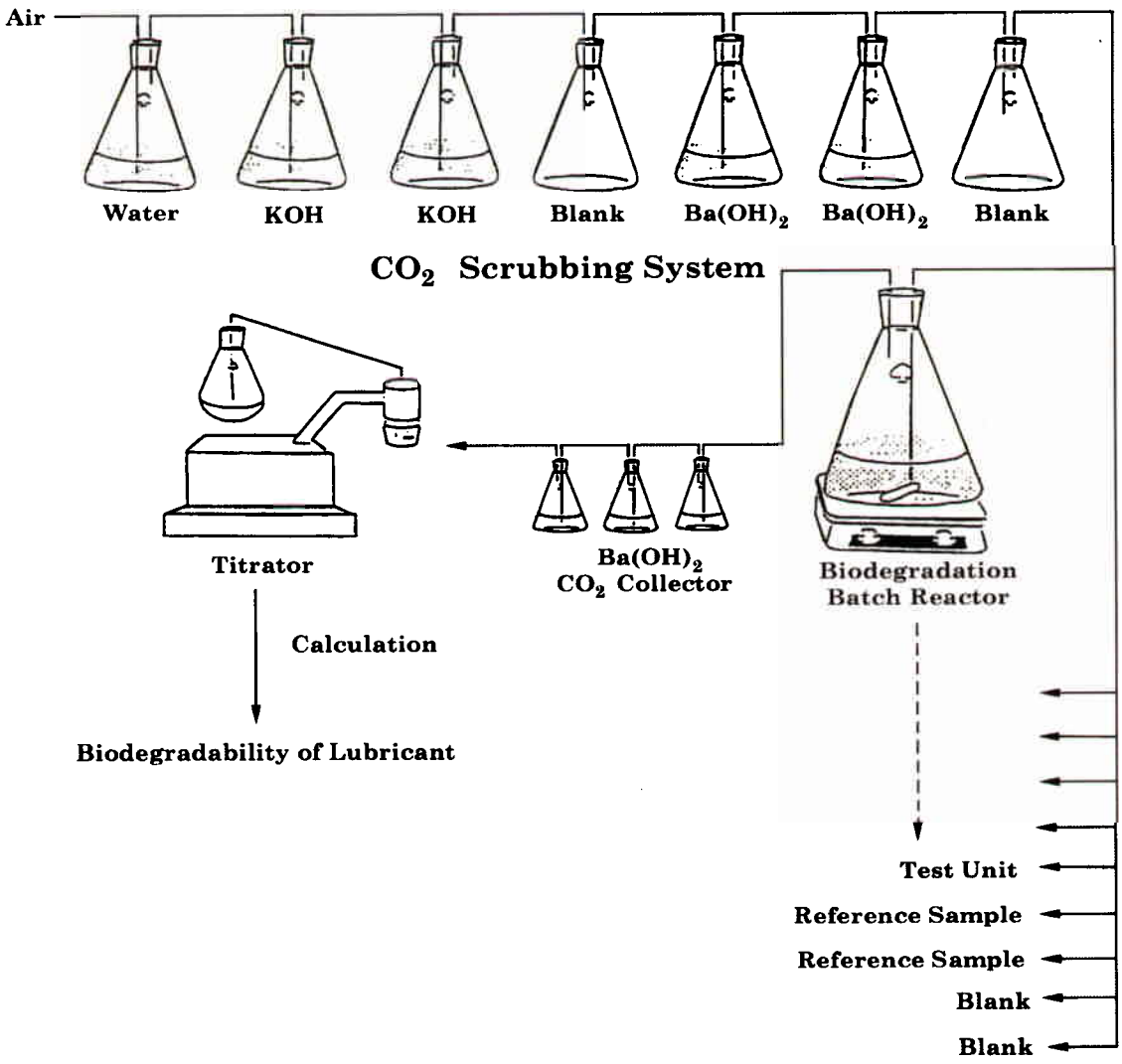
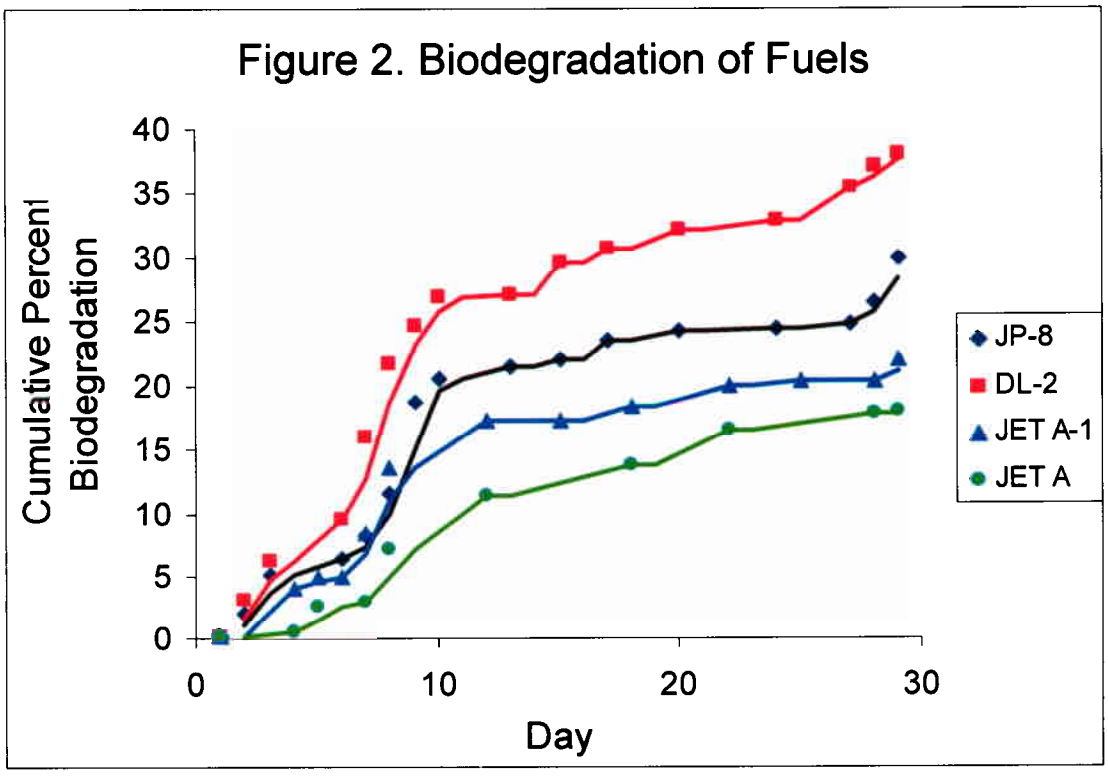


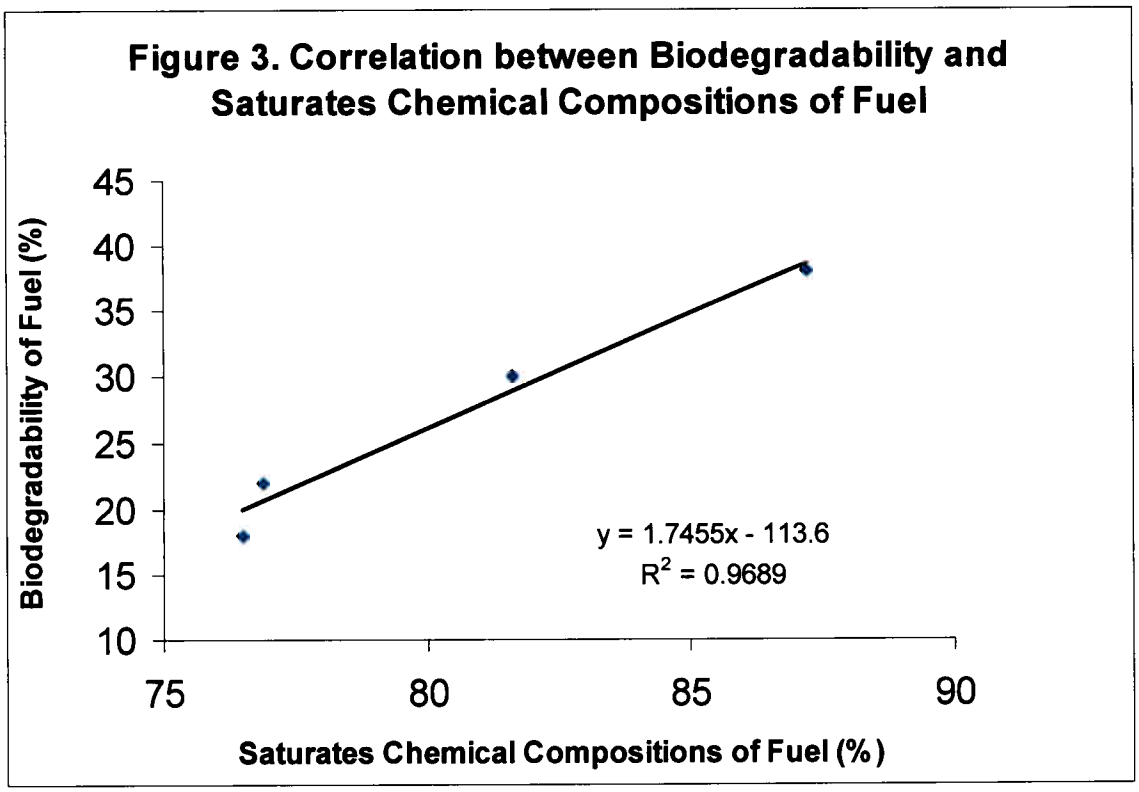
Figure 1. Schematic Diagram of Biodegradation Test Apparatus

Test Results: A summary of measured biodegradation results of four test samples is plotted in Figure 2. It is noted that these results were determined based on duplicate test results in order to increase reliability of test data and are expressed as percentage of the maximum (theoretical) carbon dioxide evolution of each test sample. Figure 2 shows that the biodegradability at 28 days ranges from 18 % to 38 %. In this test, the biodegradability of JP-8 was measured at 30 % that is slightly lower than the biodegradability of diesel fuel (38 %). The JET A provided a biodegradability of 18 %,

while JET A-1 gave 22 %. All aviation fuels exhibited lower biodegradability than the diesel fuel. In general, if a product has less than 60% of biodegradability, it is classified as a non-biodegradable product. Most petroleum based products fall in this category. Therefore, all fuels tested including JP-8 can be considered as non-biodegradable products.

It is known that the inherent biodegradability of hydrocarbon materials depends to a large extent upon their molecular structure, chemical composition, and physical properties. The chemical composition of hydrocarbon based fuels can be divided into three different chemical groups. These groups are aromatics, olefins and saturate compounds that contain paraffins and naphthenes. Typically, aromatics and olefin are slowly degradated, while straight chain aliphatic compounds are more easily degraded than aromatics. Also, unsaturated aliphatics are less readily transformed than their saturated analogues. The biodegradation test results showed that the biodegradability of tested fuels gave a good correlation with the saturated hydrocarbon group listing in Table 1. Figure 3 plots their correlation curve and the correlation coefficient was found to be 0.97. This chart also explains why diesel fuel has a higher biodegradability than aviation fuels including JP-8. In addition, the degree of biodegradability can provide a good information as to whether there is potential microbiological growth in fuel tanks or not.





The biodegradability of fuels also depends on their additive packages. A small addition of a specific chemical may drastically change the biodegradability of fuel. In addition, some toxic chemicals inhibit the growth of the microorganisms. JP-8 fuel contains three additives to improve its fuel performance. One of additives is FSII. This additive is also known as a biostat that can reduce the presence of microbiological growth. However, the biodegradation results showed that there is no evidence that FSII influences the biodegradability of JP-8 fuel. The JET A and JET A-1 are very similar to JP-8 formulation except for the additive package. Both of these fuel samples do not contain FSII. Evidently, the test results revealed that the biodegradability of both JET A and JET A-1 fuels were lower than that of JP-8. This clearly implied that the FSII did not effectively control the microbiological growth in the aquatic environment. Although JP-8 fuel has a low biodegradability, the microbiological growth is inevitable when free water is present in JP-8.

EFFICACY OF BIOCIDE ON JP-8 FUEL

Biocides are typically used in petroleum fields to control the growth of microorganisms that can cause a variety of operational problems. However, their potential to impact the environment in a negative manner can lead to concerns about where and when to use them, and can limit how much is used. For the last several decades, the U.S. Army has

used the fuel biocide agents procured under MIL-S-53021, Diesel Fuel Stabilizer Additive[7], for preventing microbiological growth in diesel fuel storage tanks, distribution systems, and vehicle/equipment fuel tanks. This biocide agent also serves as a biostat agent in fuel systems that are clean/free of water bottoms and microbiological debris. Generally, the biocide agents kills off the microorganisms and sterilizes the fuel systems, while a biostat agent inhibits further growth of microorganisms in a relatively clean fuel system, but does not necessarily sterilize the system. Commercial biocides come from a wide range of chemical types, including boron compounds, amides, imines, etc. Some of these products are effectively used, but the other products can often create compatibility problems with the additives used in the base fuel[8].

JP-8 fuel contains three different types of additives to improve its fuel performance. These additives are a corrosion inhibitor/lubricity enhancer additive, a static dissipater, and a fuel system icing inhibitor (FSII). The FSII is specified in the MIL-DTL-85470[9] (NATO Code S-1745) and is primarily intended to reduce freezing point of water precipitated from JP-8 fuel and secondarily, to reduce the tendency of microbiological growth in jet fuel. The chemical ingredient of this inhibitor is Diethylene Glycol Monomethyl Ether (DI-EGME). The recommended treatment level of this additive in either jet or diesel fuel is 0.1 to 0.15 vol %. This chemical agent is known as a biostat that is not a sterilizing agent[3]. Although it functions in the same manner as a biocide, the viable organisms still remain in the fuel system. For this reason, many military installations are often confronting problems of microbiological growth in the JP-8 storage tanks. One of the recommended solutions has been to be utilized a biocide agent for the JP-8 fuel storage tanks[10].

To determine the efficacy of a particular biocide on JP-8 fuel, a microorganism survivability test was conducted for ten days using the JP-8 fuel with/without biocide agents specified in MIL-S-53021. For the sample preparation, two 100 mL of JP-8 fuel samples were prepared in 300 mL beakers and the 20 mL of activated sludge was added in each test sample. The 0.1 % of biocide was added in one of samples. Diesel fuel and activated sludge were also prepared with the biocide for the reference samples. Then the test beakers were covered by the aluminum foil to avoid the direct sun light. Figure 4 shows the sample preparation for biocide efficacy test. In this test, each sample was cultured using the Easicult Bacteria Counting Kit for the bacteria counts. This test kit is commonly used for measuring the growth of microorganism in industrial process. For the evaluation, the cultured test kits were stored in an incubator at 27 °C. The bacteria were then counted and compared to Total Bacteria Count Agar (TTC) Chart[6] that was supplied with the test kit.

The microbiological growth in the test kits are illustrated in Figure 5, and the test results are shown in Table 2. In this test, the bacteria and fungi were counted at the beginning and the end of test. All samples inhibited with biocide tend to decrease bacteria from $1x10^5$ to $1x10^3$ cells, and there was no significant microbial reproduction in the tested samples including JP-8 fuel. It was also observed that Fungi slightly grew in all test samples. Figure 3 shows that the samples having the mixture of fuel and sludge tend to develop two layers (i.e., fuel and water phase) due to their density differences. It was

observed that the bacteria only grew in the bottom of test kit that was directly in contact with the water phase. This certainly implies that there is no microbiological growth in fuel if water is not present as a contaminant. JP-8 fuel uninhibited with biocide also tends to slightly reduce microbiological growth. It seems that DI-EGME may somewhat control the microbiological growth in JP-8 fuel. Due to the limit data, a further study is recommended to clarify the performance of DI-EGME as a biostat. However, the biocide generally reduced the microbiological growth in all samples including JP-8 fuel, but it did not completely kill the bacteria in these tests.

Table 2. Test Results from Biocide Efficacy Test for 10 days

	Bacteria count/ml	Fungi
Activated sludge	$1x10^5$	Slight
Activated sludge +Biocide	$1x10^3$	Slight
JP-8	$1x10^4$	Moderate
JP-8 + Biocide	$1x10^3$	Slight
DL-2 +Biocide	$1x10^3$	Slight

SUMMARY

1. JP-8 is a kerosene-based fuel, and its biodegradability was found to be 30 %. The biodegradability of JP-8 fuel is lower than that of diesel fuel, but it is higher than those of both JET A and JET A-1. All tested fuels have a low biodegradability and can be considered as non-biodegradable products. Their biodegradability is summarized as follow:

	JET A	JET A-1	JP-8	DL-2
Biodegradability	18 %	22%	30 %	38 %

2. JP-8 is a less biodegradable material than diesel fuel due to its higher aromatics content and lower saturate hydrocarbon (i.e., paraffin and naphthenes) content.

3. The biodegradability of fuels gave a good correlation using their saturate hydrocarbon content. The correlation equation was found based on the results obtained from the biodegradation tests.

4. The fuel system icing inhibitor (FSII) did not significantly reduce or prevent microbiological growth in JP-8 fuel.

5. Microbiological growth only occurs in the presence of free water, and at the water and JP-8 fuel interface area. It was also observed that the microorganisms did not grow in the fuel phase during the microorganism survivability tests.

6. The biocide used in diesel fuel tends to kill those microorganisms that were present in JP-8 fuel. Their performance is very similar to that observed in diesel fuel. The biocide also produces a significant amount of biomass residue/debris in the bottom of test beaker due to its insolubility in either the water or the fuel. This implies that the free water contaminated by the microorganisms can separated from the bottom of actual fuel tank environments. The biomass residue/debris must subsequently be removed to avoid filterability and clogging problems of the fuel system.

7. Even though JP-8 fuel has a low biodegradability, it still allows microbiological growth to occur whenever free water is present in the fuel.

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Figure 4. Sample Preparation for Biocide Efficacy Test

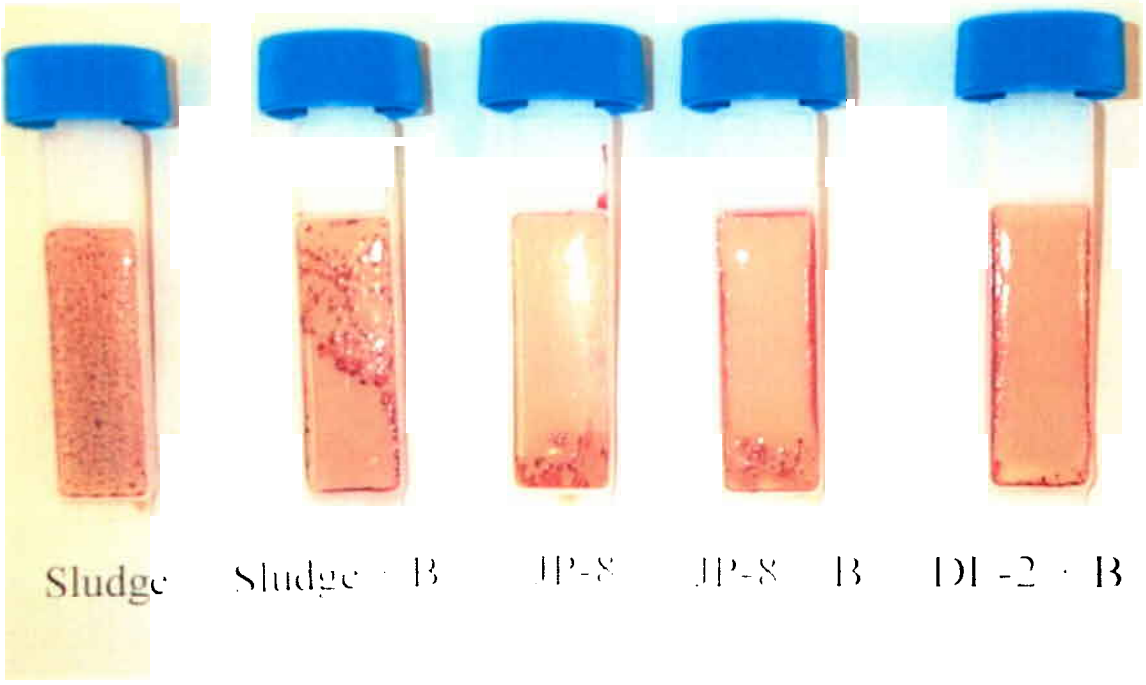

Figure 5. Microbial Growth in the Easicult Bacteria Test Kits